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Nosé-Hoover molecular-dynamics study of self-pipe-diffusion in gold using many-atom interactions

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Self-diffusion along the [112] Shockley parital dislocation pair (self-pipe-diffusion) in Au is studied with Nosé-Hoover molecular dynamics (MD) using the many-atom Ackland-Tichy-Vitek-Finnis model. We find the following formation energy difference between interstitials (i) and vacancies (v) at partial dislocations: $\Delta E_f = E_f(i) - E_f(v) = 1.3$ eV. Thermal disorder in the stacking fault region makes it difficult (or even impossible) to follow the migration of single vacancies or interstitials sufficiently long times in the temperature range $0.78T_m \ldots T_m$ ($T_m = 1475$ K is the melting temperature). The diffusion induced by one vacancy and one interstitial calculated at the temperature range 1150–1400 K gives the following migration energies: $E_m(v) = 0.75$ eV and $E_m(i) \approx 0.0$ eV. Since the activation energy for interstitials is about 0.5 eV larger than that for vacancies, self-pipe-diffusion is more vacancy type than interstitial type. The components of the induced diffusion constants indicate the spread of diffusion into the whole stacking fault region.

Enhanced self-diffusion in metals occurs near extended defects such as surfaces, grain boundaries, and dislocations. In fcc metals the energetically most favorable edge dislocations appear in the [112] direction as pairs of Shockley partial dislocations with an hcp stacking fault ribbon in between.[1] Self-diffusion along dislocations—called here self-pipe-diffusion—is usually studied experimentally by measuring tracer diffusion along low-angle grain boundaries.[2] However, it is difficult to answer by experiments alone the following fundamental questions. What is the main mechanism for self-pipe-diffusion: vacancies, interstitials, or something else?[1-4] What is the reason for the following general trend observed in metals: self-pipe-diffusion in Shockley pairs is weaker than in perfect dislocations?[2-4]

According to the argument by Friedel[1] self-pipe-diffusion should be due to vacancies because interstitials may be expected to find sites close to the dislocations where the interstitials will be more stable than in the bulk. Another argument for the vacancy mechanism is the fact that the activation energy for the interstitial mechanism is significantly larger than that for the vacancy one in the bulk and the vicinity of a dislocation is not expected to reduce this difference sufficiently. The majority of later studies including the atomistic simulations in the pair-potential approximation (PPA) prefer the vacancy mechanism.[2,5] However, a recent molecular-dynamics (MD) simulation for Cu, using the PPA, gave the variant and surprising result that vacancies and interstitials contribute comparably to self-pipe-diffusion.[3,4]

The general trend that self-pipe-diffusion in Shockley pairs is weaker than in perfect dislocations is attributed either to the decreased Burgers vectors of the Shockley partial dislocations[2] or to the spread of self-pipe-diffusion into the whole stacking fault region.[6] The MD simulation for Cu favors the latter explanation.[3,4]

The purpose of this paper is to shed light on the above questions by presenting results from constant-NVT MD simulations of self-pipe-diffusion in Au using semiempirical *many-atom* forces of the Akland-Tichy-Vitek-Finnis (ATVF) model[7] (N is the number of atoms, V is the volume and T is the temperature). In this model the total energy is written in the form

$$\mathcal{V} = \frac{1}{2} \sum_{\substack{i,j=1 \\ (j \neq i)}}^{N} \Phi(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^{N} U(n_i) , \tag{1}$$

where

$$n_i = \sum_{\substack{j=1 \\ (j \neq i)}}^{N} \rho(|\mathbf{r}_i - \mathbf{r}_j|) . \tag{2}$$

In Eqs. (1) and (2) Φ is a repulsive pair potential, $\mathbf{r}_i$ is the position vector of nucleus i, and U is an attractive many-atom potential. U has the form $U = -n_i^{1/2}$ derived from the tight-binding approximation, n_i is the second moment of the density of states, and ρ is an empirical short-range radial function.[7] The force $-\nabla_i \mathcal{V}$ acting on nucleus i is as follows:

$$\mathbf{f}_i = -\sum_{j(\neq i)} \{\Phi'(|\mathbf{r}_i - \mathbf{r}_j|) + [U'(n_i) + U'(n_j)]\rho'(|\mathbf{r}_i - \mathbf{r}_j|)\} \times \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|} , \tag{3}$$

where $'$ denotes a derivative with respect to the argument.

The initial configuration was obtained as follows. First the Cotterill-Doyama recipe[8] was used to create two extra half-planes of atoms symmetrically in the center of the system and to displace the atoms according to the isotropic elasticity theory.[9,10] Then by using fixed boundaries in the x and y directions and periodic boundaries in the z direction (the [112] direction of the Shockley par-

tial dislocations) the system of 4683 movable and 3324 fixed atoms was allowed to relax. This was accomplished by using constant-NVT MD at $T=1$ K, i.e., by solving the Nosé-Hoover equations of motion[11-13]

$$\frac{d^2\mathbf{r}_i}{dt^2}=\frac{1}{m}\mathbf{f}_i-\xi\mathbf{v}_i\ , \tag{4}$$

$$\frac{d\xi}{dt}=\frac{1}{\mathcal{Q}}\left[\sum_i m\mathbf{v}_i^2-n_f k_B T\right]\ , \tag{5}$$

where m and $\mathbf{v}_i$ denote the mass and velocity of atom i, respectively, ξ is the friction coefficient keeping the temperature of the system at fixed T, $\mathcal{Q}$ is the thermal inertia parameter, n_f denotes the number of degrees of freedom, and k_B is Boltzmann's constant. A modified velocity-Verlet algorithm with a time step of 2.5 fs was used to solve Eqs. (4) and (5).[14] This procedure results in the configuration shown in Fig. 1 with a partial separation of about 38 Å.

The vacancy and interstitial formation energies at the edge of the partial dislocation [$E_f(v)$ and $E_f(i)$, respectively] are obtained by performing constant-NVT MD at $T=1$ K with $N\mp1$ particles and calculating the appropriate energy differences from the equation

$$\Delta\mathcal{V}=\mathcal{V}(N\mp1)-(N\mp1)\mathcal{V}(N)/N \tag{6}$$

including now all relaxations ($N=8007$, number of movable atoms $=4683\mp1$). As the result we get $E_f(v)=1.4$ eV and $E_f(i)=2.7$ eV. The formation energy difference $E_f(i)-E_f(v)=1.3$ eV is thus significantly reduced from the value in the crystal: $E_f^{\rm cr}(i)-E_f^{\rm cr}(v)=(4.35-0.96)$ eV $=3.39$ eV.[7] However, while the interstitial formation energy is reduced from 4.35 to 2.7 eV, the vacancy formation energy is increased from 0.96 to 1.4 eV. Instead of this increase usually a small decrease is obtained: 0.14 eV for Au (Ref. 5) and 0.27 eV,[5] 0.37 eV,[3,4] and 0.14 eV (Ref. 16) for Cu. Also we find using the many-atom glue model[17] a decrease by 0.49 eV for Au. We may think of two reasons for this. First, the results in Ref. 7 are obtained for a periodic crystal with a conjugate gradient method differing from our method. Second, the formation energies are calculated as a difference of two large numbers. However, we think that the relative sizes of our $E_f(i)$, and $E_f(v)$ are more meaningful in the comparison than their absolute values because essentially the same $\mathcal{V}(N)$ is subtracted in both cases [Eq. (6)].

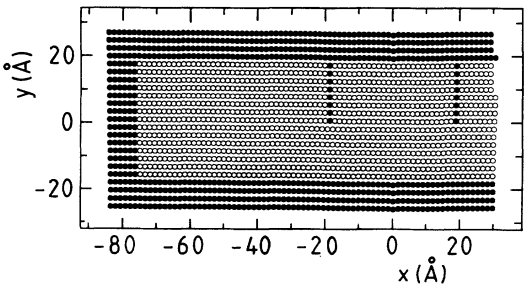

FIG. 1. The xy projection of the initial configuration for Au at $T=1$ K. The z axis is the [112] direction and the xz plane is the $(11\bar{1})$ plane. The filled circles represent the fixed atoms of the boundary layer and the open circles the movable atoms except that the two chains of filled circles represent the movable atoms of the two extra half-planes forming the Shockley pair. The configuration is symmetric with respect to the yz plane.

The migration of vacancies and interstitials can be calculated only close to the melting temperature T_m [for the ATVF model $T_m=1475$ K (Ref. 15) and the experimental $T_m=1336$ K]. The heating of the ATVF system must proceed slowly because a fast heating rate always would result in disordered and even melted regions around the stacking fault. Therefore we increased temperature T by increments of 50 K and simultaneously scaled the system according to thermal expansion.[15] Typically several thousand to 10 000 time steps were used to equilibrate the system at each T. Above 1000 K a smaller increment of 25 K was used. Although the atomic arrangement at $T=1150\ldots1400$ K is less regular than at $T=0$ K the partial dislocations are still discernible.

Since the stacking fault region has lower symmetry than the crystal we monitored the migration of a vacancy and an interstitial by using the following *coordination density* method. A bell-shaped density profile of the form

$$\rho(r)=\left[1-2\left[\frac{r}{c}\right]^2+\left[\frac{r}{c}\right]^4\right]\cdot\theta(c-r) \tag{7}$$

was placed at each atom (the constant $c=3.0$ Å is slightly larger than half of the nearest-neighbor separation, r is the distance from the nucleus, and θ is the Heaviside step function). The coordination density ρ_t is calculated as the sum of the atomic contributions:

$$\rho_t(\mathbf{r})=\sum_{i=1}^{N}\rho(|\mathbf{r}-\mathbf{r}_i|)\ . \tag{8}$$

The minimum of ρ_t locates a vacancy. However, this minimum is meaningful only if it does not exceed a typical minimum value of ρ_t in a regular Au crystal between the atoms (this value equals 0.9). In the calculations the vacancy is surrounded by a sphere of radius R plus a "skin" and only the atoms inside this region contribute to ρ_t (analogously to the use of Verlet's neighbor list). ρ_t is calculated at the intervals $R/10$ inside the sphere at the time intervals $4\times\delta t=10$ fs.

The location of an interstitial is calculated in an analogous way. The interstitial is now located at the nucleus where ρ_t attains its maximum value. However, this maximum is meaningful only if it exceeds the value of ρ_t at a typical atom of the crystal (this value equals 2.3).

A vacancy created at the left partial dislocation could be followed for ~60 ps at $T=1300$ and 1400 K. Although the numbers of jumps (4 and 6) are not statistically sufficient one can nevertheless—assuming the Arrhenius-type behavior—derive an estimate for the vacancy-migration energy: $E_m(v)\approx0.5$ eV. An interstitial created in front of the left partial dislocation could be followed only for ~100 fs. During this time the role of the interstitial changed from one atom to another 1, 2, and 4 times at $T=1150$, 1300, and 1400 K, respectively. This indicates that the interstitial migration energy $E_m(i)$ is small. However, these calculations show that disorder caused by thermal motion especially in the stacking fault region at the temperatures $1150\ \text{K}<T<T_m$ makes it difficult (or even impossible) to follow the migration of

single vacancies or interstitials sufficiently long times.

To circumvent the above difficulties we have calculated directly the net mass transport induced by one vacancy or one interstitial. In our calculations either one atom is removed from each partial dislocation edge or one atom is added in front of each dislocation edge. The (one) vacancy and (one) interstitial diffusion constants are then calculated from the equations

$$D_v = \tfrac{1}{2}[D(N-2)-D(N)] , \tag{9}$$

$$D_i = \tfrac{1}{2}[D(N+2)-D(N)] , \tag{10}$$

where

$$D(N) \overset{t\to\infty}{=} \frac{1}{6t} \sum_{i=1}^{N} [\mathbf{r}_i(t)-\mathbf{r}_i(0)]^2 . \tag{11}$$

The calculations of ~ 1.5 ns each give the results shown in Fig. 2, presented as $\ln(D_v/D_0)$ and $\ln(D_i/D_0)$ versus $(k_B T)^{-1}$. The diffusion induced by one interstitial is 3–16 times as large as that induced by one vacancy. The reason for the anomalously low value of D_i (1400 K) is not clear to us but may be related to the fact that the initial configuration used at 1400 K had a significantly longer equilibration time than the initial configurations at 1150 and 1300 K. Another possibility would be that the diffusion induced by the interstitial penetrates to regions of low migration (e.g., bulk crystal; this behavior was found in Ref. 4 for vacancies). Least-squares fits to the Arrhenius law (the two lines in Fig. 2) give for the vacancy and interstitial migration energies the values $E_m(v)=0.75$ eV and $E_m(i)=-0.14$ eV, respectively. The value of $E_m(i)$ is unphysical but clearly indicates that $E_m(i)$ is very small. Nevertheless, although $E_m(i)-E_m(v)\approx -0.75$ eV, $\Delta E_f = E_f(i)-E_f(v)=1.3$ eV, which makes the activation energy for interstitial self-diffusion about 0.5 eV larger than for the vacancy mechanism. Thus ΔE_f does not decrease enough at the dislocation line compared to the bulk to make the interstitial-type diffusion competitive with the vacancy-type diffusion. In this respect our result for Au differs from the MD result in PPA for Cu.[3,4]

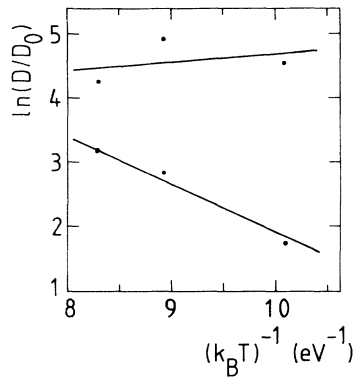

FIG. 2. Vacancy (lower data points) and interstitial (upper data points) diffusion constants D, defined in Eqs. (9) and (10). $\ln(D/D_0)$ versus $(k_B T)^{-1}$ is presented where $D_0=4.68\times 10^{-7}$ cm^2/s, k_B is Boltzmann's constant and T is temperature. The diffusion is simulated at 1150, 1300, and 1400 K.

We find that the x and z components of the induced diffusion constants are roughly of the same size and larger than the corresponding y components. This indicates the spread of self-diffusion into the whole stacking fault region.

In conclusion, thermal disorder in the stacking fault region makes it difficult (or even impossible) to follow the migration of single vacancies or interstitials sufficiently long times at 1150 K $< T < T_m$. By calculating directly the diffusion constants from the net mass transport induced by one vacancy and one interstitial we find—combining with the corresponding formation energies—that self-pipe-diffusion in Au is more vacancy type than interstitial type. The calculated x and z components of the induced diffusion constants are similar in size and larger than the corresponding y components. This indicates that the reason for the observed general trend in metals that self-pipe-diffusion in partial dislocation pairs is weaker in perfect dislocations is the spread of diffusion into the whole stacking fault region.

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